

**MATHEMATICAL MODELLING OF SOLAR ULTRAVIOLET RADIATION
INDUCED OPTICAL DEGRADATION IN ANODIZED ALUMINUM**

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ABSTRACT

In the design of spacecraft for proper thermal balance, accurate information on the long-term optical behavior of the spacecraft outer skin materials is necessary. This paper presents a phenomenological model for such behavior, explains the underlying principles involved, and gives some examples of the model's fit to actual measurements under simulated earth-orbit conditions. The paper concludes with some comments on applicability of the model to materials testing and thermal modelling.

INTRODUCTION

Since the early 1960's, a considerable body of data has been acquired on the performance of Alzak¹ anodized aluminum under simulated space radiation conditions. This material has generally poor space stability, but is unique in that it demonstrates a consistent, repeatable deterioration in optical properties when exposed to ultraviolet radiation in vacuum². This characteristic makes it an ideal reference material for validation of space simulation facility performance.

In 1981, major modifications to the AFWAL/ML³ SCEPTRE (Space Combined Effects Primary Test Research Equipment) began, with a goal of raising the then-inadequate (.2 UV sun) simulated solar intensity to a useful (>1.0 sun) level, and .1 mil Alzak was decided upon as a control material. By 1985, this effort had been concluded, which provided a unique opportunity to examine Alzak behavior under simulated solar UV intensities in the range 0-1 sun. Examination of the historical record provided further information from an earlier work⁴ which has extended this data set to 3 suns (SCEPTRE data at >1 sun intensity has been in a combined UV/electron environment). Thus, data is available for an extremely wide intensity range under known conditions with a known material.

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¹A product of Alcoa Corporation

²"Proceedings of the International Symposium on Solar Radiation Simulation" - IES/ASTM, January 1965, pps. 115-122.

³Air Force Wright Aeronautical Laboratories/Materials Laboratory

⁴"Effects of Vacuum-Ultraviolet Environment on Optical Properties of Bright Anodized aluminum Temperature Control Coatings," AFML-TR-67-421, J. H. Weaver, AFML, May 1968.

The desire to understand the material behavior arises from the need for space simulation testing to be conducted under accelerated conditions, i.e. at intensities greater than those experienced in the actual flight environment. Testing is usually conducted at intensities for 2-10 suns, and then "scaled" by multiplying the test time against the intensity to yield what is presumed to be a useful dose measurement, generally called "Equivalent Sun-Hours" or ESH. The unstated assumption in such scaling is that of Reciprocity - that a reciprocal relationship exists between the intensity and the time constant for material damage, with no significant deviation in total damage to the material.

The SCEPTRE tests of Alzak do not bear out this assumption. While data from individual test runs can be nicely fitted to a "french curve" asymptotic trace (Figure 1), when the data is expressed in terms of the total dose in ESH, any such relationship disappears (Figure 2). This suggests that a more complicated relationship between time, intensity, and damage occurs.

It is the intent of this paper to express, as completely as possible, that relationship.

DERIVATION OF THE MATH MODEL

Consider a monomolecular layer of Alzak containing some number N_0 of possible sites for color center formation. Figure 3 illustrates the behavior of such a layer when exposed to ionizing radiation at an intensity of 3 ionizing photons/unit area/unit time. One photon interacts with a site, forming a color center. Another photon interacts with an existing color center - and has no effect. The last photon passes through the layer without effect, presumably to create a color center deeper in the material.

Our objective is to derive an equation which will define the concentration of color centers in this layer as a function of time.

$$\frac{d}{dt} \left(\frac{N(t)}{N_0} \right) = \sigma \left(\frac{N_0 - N(t)}{N_0} \right) I_0 \quad (1)$$

this equation is satisfied by $N(t)$ defined as

$$N(t) = N_0 (1 - e^{-t/\tau}) ; \tau = \frac{1}{\sigma I_0} \quad (2)$$

which may be divided through by N_0 to yield the concentration of color centers as a function of time

$$\frac{N(t)}{N_0} = 1 - e^{-t/\tau} \quad (3)$$

The observable value related to the concentration of color centers is the solar absorptance ($\alpha_s(t)$), which may be found by

$$\alpha_s(t) = \alpha_0(N_0 - N(t)) + \alpha_1(N(t)) \quad (4)$$

Subtraction of the initial value yields the change in solar absorptance as a function of time

$$\Delta\alpha_s(t) = \alpha_s(t) - \alpha_o = \alpha_1(1 - e^{-t/\tau}) \quad (5)$$

Now this model is very interesting, despite its flaws, since this is the model implied by the assumption of linear reciprocity stated in the introduction. Indeed, a 100 hour exposure to radiation at 2 UV sun intensity should, according to this model, have exactly the same effect as 200 hours of exposure at 1 UV sun.

Attempting to fit the observed data to this model yields Figure 4. Clearly the model fails - and the most obvious way in which it could fail is by assuming that all the damage occurs in a single monolayer of material.

Therefore, let us consider a multi-layer model.

Figure 5 illustrates such a model, which is essentially a stack of monolayers as defined in Figure 3, viewed from the side. Again, we see three incident photons. One forms a color center in layer one, one impacts an existing center without effect, and the third passes through to create a new center in layer 2. The difference between this case and the monolayer case is now clear - at heightened intensities, damage will be done deeper in the material, so the total saturation value for color center concentration (and, by inference, solar absorptance) will be higher.

The model is described by

$$\frac{\partial}{\partial t} \left| \frac{N(x,t)}{N_o} \right| = \sigma \left(\frac{N_o - N(x,t)}{N_o} \right) I(x) ; I(x) = I_o e^{-ax} \quad (6)$$

which is satisfied by

$$N(x,t) = N_o (1 - e^{-t/\tau(x)}) ; \tau(x) = \frac{1}{\sigma I(x)} \quad (7)$$

Dividing through by N_o yields the Color Center Concentration

$$\frac{N(x,t)}{N_o} = 1 - e^{-t/\tau(x)} \quad (8)$$

This completes the derivation of the model, but does not yield an observable quantity. To get an observable ($\alpha_s(t)$) from this, we again apply Equation (4), noting this time that we must integrate over the thickness of the material, which leads to

$$\alpha_s(t) = \frac{\alpha_o \int_0^D [N_o - N(x,t)] dx + \alpha_1 \int_0^D N(x,t) dx}{\int_0^{D*} N_o dx} \quad (9)$$

rearranging terms, and integrating the simpler ones yields

$$\alpha_s(t) = \frac{\alpha_o N_o D + (\alpha_1 - \alpha_o) \int_0^D N_o (1 - e^{-\sigma t I_o e^{-ax}}) dx}{N_o D} \quad (10)$$

This cannot be analytically solved for all time, but it can be solved for the trivial case of $t=0$ (yielding α_0 , as expected), and for the limit as time goes to infinity. This last yields

$$\lim_{t \rightarrow \infty} [\alpha_s(t)] = \frac{\alpha_0 N_0 D + (\alpha_1 - \alpha_0) N_0 d_1}{N_0 D} \quad (11)$$

Where we note that at depths greater than d_1 , no color centers are formed, so the integral range for the $N(x,t)$ term is thus restricted. Cancelling the N_0 's yields

$$\lim_{t \rightarrow \infty} [\alpha_s(t)] = \alpha_0 + (\alpha_1 - \alpha_0) \frac{d_1}{D} \quad (12)$$

And subtraction of the α_0 yields

$$\Delta \alpha_s = \alpha_s - \alpha_0 = (\alpha_1 - \alpha_0) \frac{d_1}{D} \quad (13)$$

Which expresses the total change in absorptance over infinite time. It merely remains to find the maximum depth of damage d . We do this by applying Beer's Law to compute the intensity at the maximum depth.

$$I(x) \Big|_{x=d_1} = I(d_1) = I_0 e^{-ad_1} \quad (14)$$

Taking the log of both sides, noting that the threshold intensity at the depth of maximum damage must be a constant (since at greater depths it is quantum-mechanically improbable that there will be any effect) and solving for d_1 yields

$$d_1 = A \ln(I_0) + B \quad (15)$$

where A and B are arbitrary constants. Substituting this back into Equation (12) and combining constants yields

$$\begin{aligned} \lim_{t \rightarrow \infty} \Delta \alpha_s(t) &= (\alpha_1 - \alpha_0) (A \ln(I_0) + B) / D \\ &= A \ln(I_0) + B \end{aligned} \quad (16)$$

We now make the assumption that the complete, time-dependent equation can be separated into static and dynamic components, of which Equation (16) is the static component

$$\begin{aligned} \Delta \alpha_s(t) &= [\Delta \alpha(t)] f(t) \\ &= (A \ln(I_0) + B) f(t) \end{aligned} \quad (17)$$

Inspection of Equation (10) yields the dynamic (time-dependent) component

$$f(t) = K \int_0^{d_1} [1 - e^{-t/\tau(x)}] dx; \quad \tau(x) = \sigma t_0 e^{-ax} \quad (18)$$

Which has no analytical solution. We approximate this function by converting it to series form

$$f(t) \approx K \sum_{i=1}^n (1-e^{-t/\tau(x)})^{\Delta x} ; x=\Delta x(i-1); \quad (19)$$

$$\tau(x) = \sigma I_o e^{-a\Delta x(i-1)}$$

And then note that the most significant term is the first, due to the nature of the exponential component. Truncation of all terms for $i>1$ yields

$$f(t) \approx K(1-e^{-t/\tau}) ; \tau = \frac{1}{\sigma I_o} \quad (20)$$

where K is an arbitrary constant. Substitution back into Equation (17), and combination of the constants finally yields

$$\Delta\alpha_s(t) = [\Delta\alpha_s(t)]_{\infty} f(t) = a_1(I_o)(1-e^{-t/\tau(I_o)})$$

$$\tau(I_o) = \frac{1}{\sigma I_o} = \frac{k}{I_o}$$

$$a_1(I_o) = A \ln(I_o) + B$$

where $\sigma, A, B = \text{constant}$ (21)

Which represents an approximate expression for the observable variable - the change in solar absorptance.

TESTING THE MODEL AGAINST REALITY

Figures 6 and 7 illustrate that, indeed, τ is inversely proportional to intensity, and a_1 is linear with the log of the intensity. Simple least-squares fitting produces the constants in question, thus

$$\tau = 95.0/I$$

$$a_1 = .008 \log(I) + .042$$

(or $k=95$, $A=.008$, $B=.042$ in the nomenclature of Eq. (21))

Substituting these into Equation (21) and plotting for the actual test intensities of .2, .5, 1.0, and 3.0 suns yields Figure 8 - which shows that the equation does indeed fit the data to within the illustrated error limit of $\pm .005$ in α_s .

This data fit is far too close to be fortuitous - if this model is not accurate, it is at least much closer than the naive model illustrated in Figure 4.

CONCLUSION - IMPLICATIONS ARISING FROM THE MODEL

Given that Equation (21) provides a working approximation to material behavior in this case, we are left with several interesting questions:

1 - Does the model apply to other materials?

We do not know. Existing SCEPTRE data sets for materials other than Alzak encompass at best two exposure intensities, which is insufficient to validate linearity of a_1 and τ . However, if an iterative solution for a_1 and τ is tolerated, every data set we have, for organic and inorganic paints, OSR's, etc. can be fitted to Equation (8). This procedure yields a resultant function which is valid only at the intensity for which data is available, but it is nonetheless encouraging.

2 - Does the model apply to other radiation environments?

Again, insufficient data prevents us from making a definitive answer, but the iterative procedure mentioned above has so far been successful at producing a fit to within experimental error limits for all SCEPTRE UV/vacuum and UV/vacuum/electron tests.

3 - Assuming that the model is (at least approximately) valid, what does it say about present-day accelerated testing of spacecraft materials for space stability?

The model has several implications for accelerated testing, well expressed by comparing Figures 4 and 8. The assumption that test results can be corrected for varying intensity by scaling the time axis is clearly false. It does appear, however, that testing at accelerated intensities represents a "safe worst case", since the saturation value is always higher for higher intensity.

Perhaps the most important implications are for intercomparison of ground-based simulation data to flight test results. When those of us in the simulation community speak of a "UV-sun" we mean an equivalent UV intensity to that from the sun, assuming a view factor of 1.0 = with the specimen normal to the incident light ray. In the real environment, for most any condition, view factor considerations will lead to a time-averaged intensity of less than .5 UV-suns for a real spacecraft on-orbit. If the simulation testing has been conducted at 2 suns, then the acceleration factor will be 4, not 2 as is often claimed. Given the intensity dependent nature of Equation (21), this suggests that such comparisons need to be examined very carefully - and leads one to question exactly what is meant if ground test results at high acceleration factors do indeed match flight test data. Given the prediction that tests at accelerated intensity will always yield more damage than a lower intensity, one is left to wonder which non-modeled component of the flight environment is responsible for the implied additional damage, and which materials are susceptible to its effects.

If Equation (21) does prove applicable to other materials and other environments, then it may become possible to answer some of these questions, and to put modern ground-based space environmental effects testing on a more sound theoretical footing. In this regard, it should be noted that the models defined by Equations (1) - (21) are in fact special cases of a model defined by Equation (22),

$$\frac{\partial}{\partial t} \frac{N(x,t)}{N_0} = \sigma(x,t) \frac{N_0 - N(x,t)}{N_0} I(x,t) \quad (22)$$

In which both the incident radiation intensity and the cross-section are defined as functions of both depth and time. If solutions - whether exact or approximate - can be found for this model, then it may well prove possible to generalize the work described herein to more complex systems and conditions.

REFERENCES

1. "Proceedings of the International Symposium on Solar Radiation Simulation," IES/ASTM, January 1965.
2. "Effects of Vacuum-Ultraviolet Environment on Optical Properties of Bright Anodized Aluminum Temperature Control Coatings," AFML-TR-67-42), J. H. Weaver, AFML, May 1968.

SYMBOLS

t	time (hrs)
$N(t)$	number of cells in a given monolayer changed up to time= t
N_o	number of cells per monolayer
$N(t)$ total	total number of cells changed at time= t
α_s	solar absorptance (absorptance units)
α_o	initial solar absorptance (absorptance units)
α_l	final solar absorptance (absorptance units)
σ	radiation effectiveness cross-section (fraction)
k, A, B, a_l	arbitrary constants
τ	time constant (hrs)
I_o	surface radiation intensity
I_i	radiation intensity at layer i
n	number of layers to which radiation penetrates
i	index of a given layer
Δd	thickness of a single layer of material
d_l	maximum depth to which radiation penetrates
a	optical density of material at radiation wavelength
D	total thickness of material

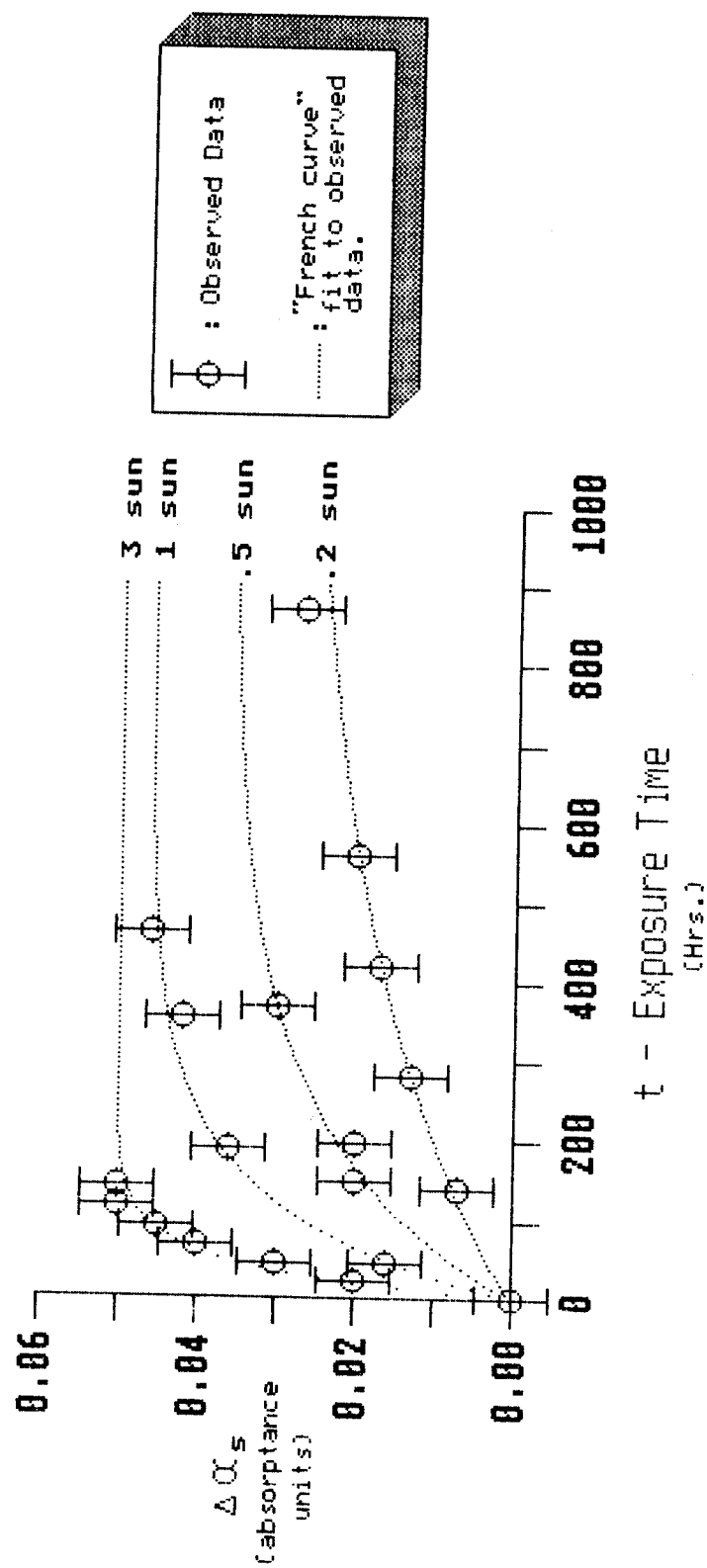


Figure 1. Alzak data for various intensities

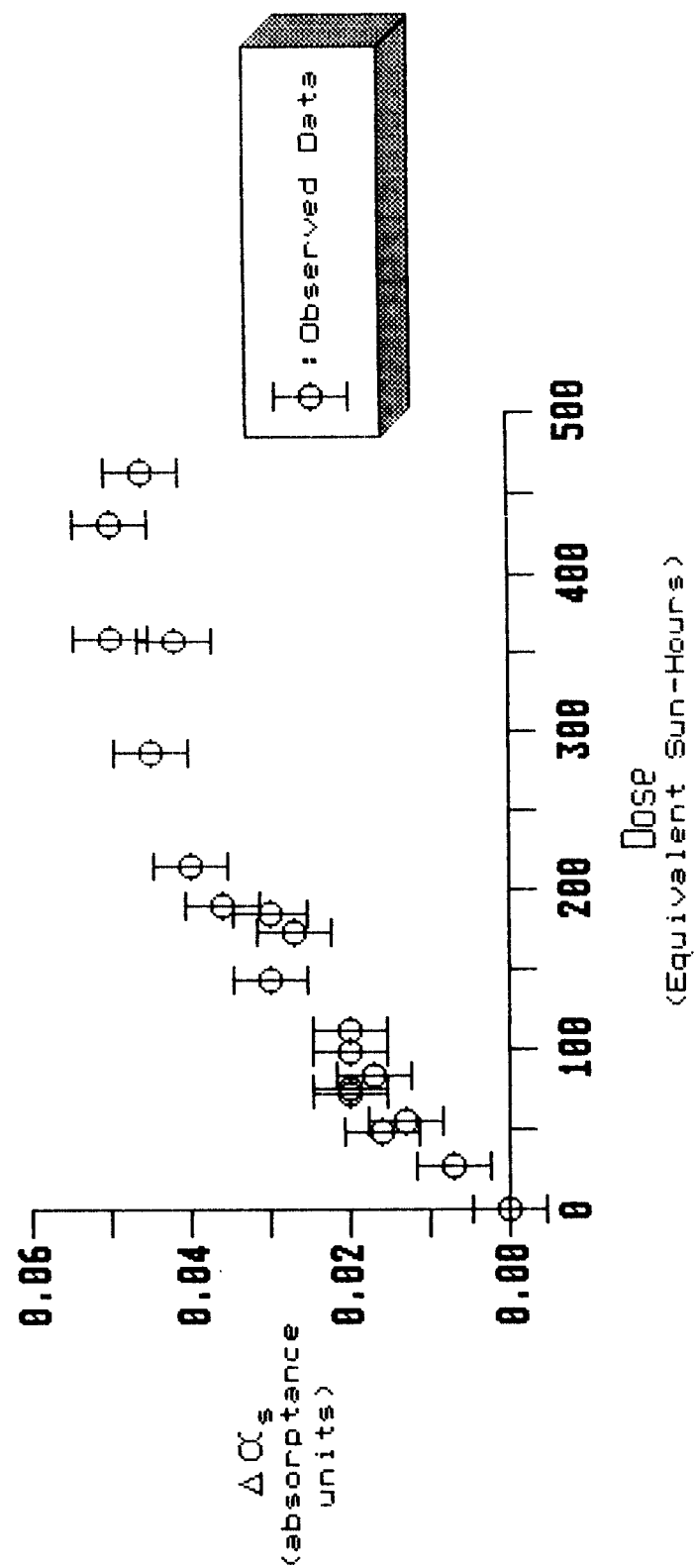


Figure 2. Degradation vs. dose - no simple relationship

c

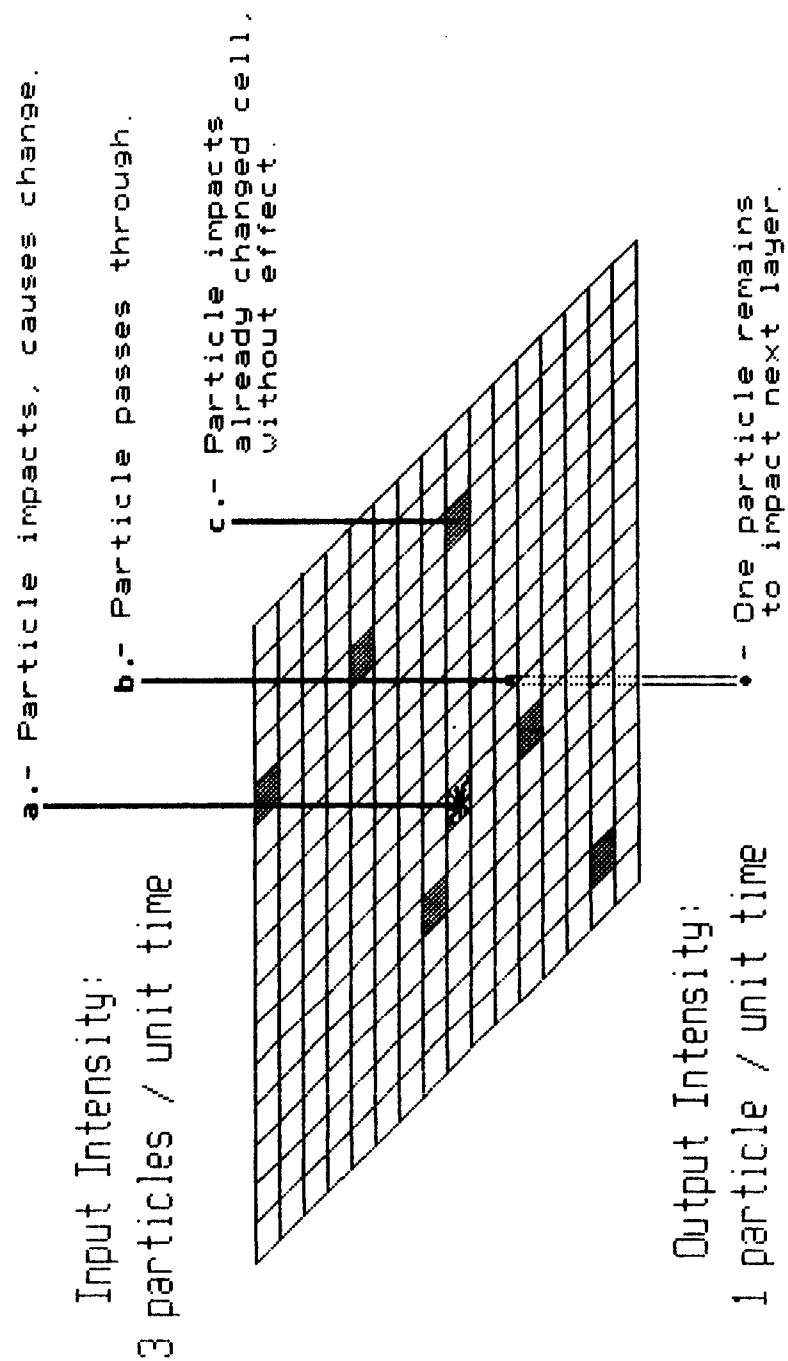


Figure 3. Degradation phenomena in one monolayer

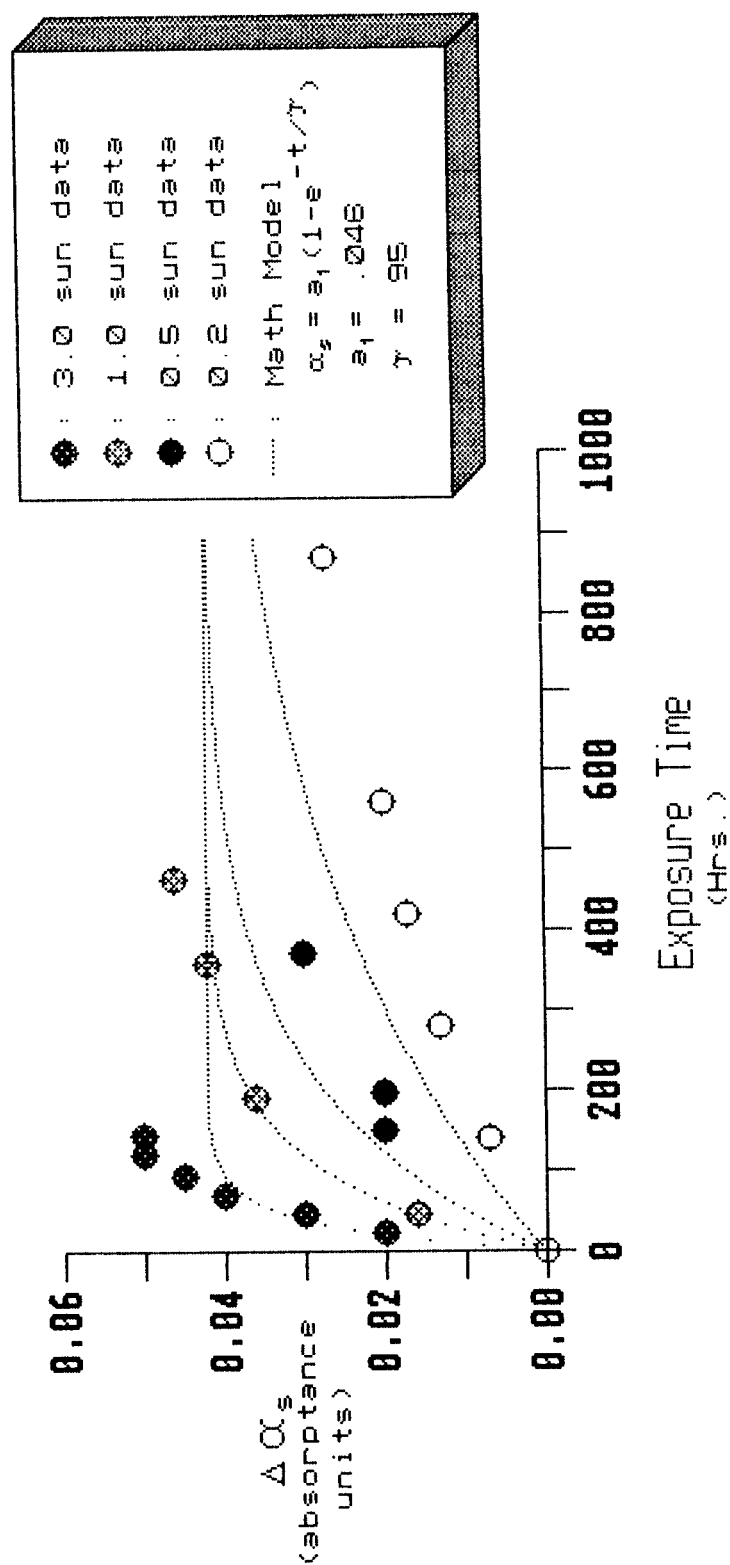
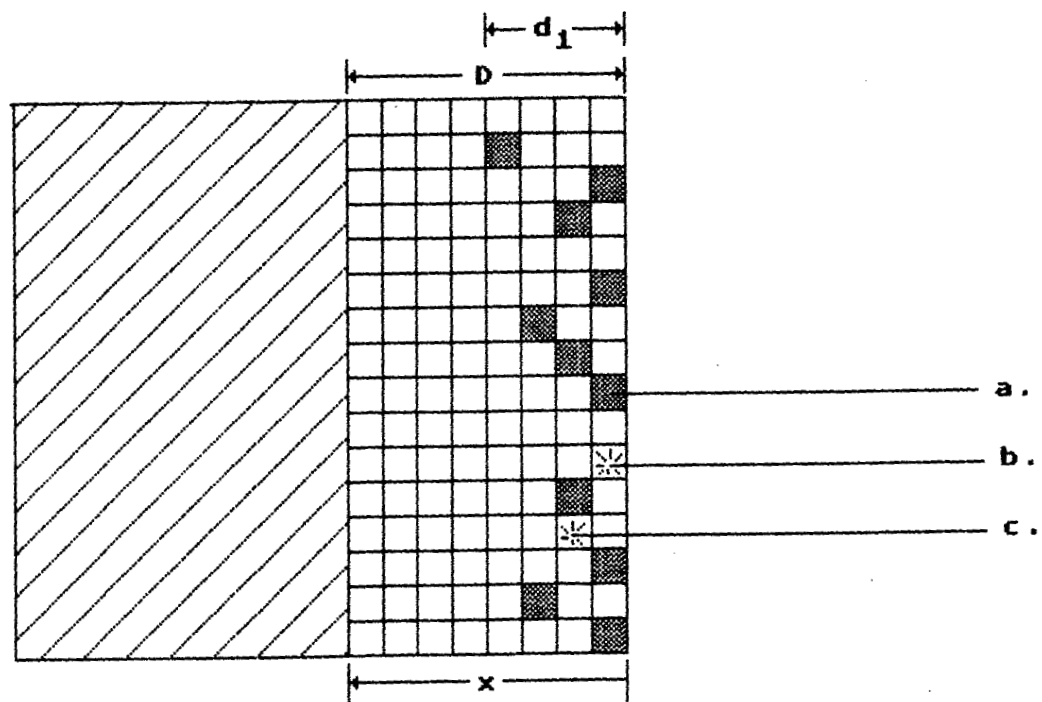


Figure 4. "Naive" monolayer math model



$$\text{Model: } \left. \frac{\partial}{\partial t} \right|_x \frac{N(x,t)}{N_0} = \sigma \frac{N_0 - N(x,t)}{N_0} I(x)$$

Figure 5. Color center generation in depth

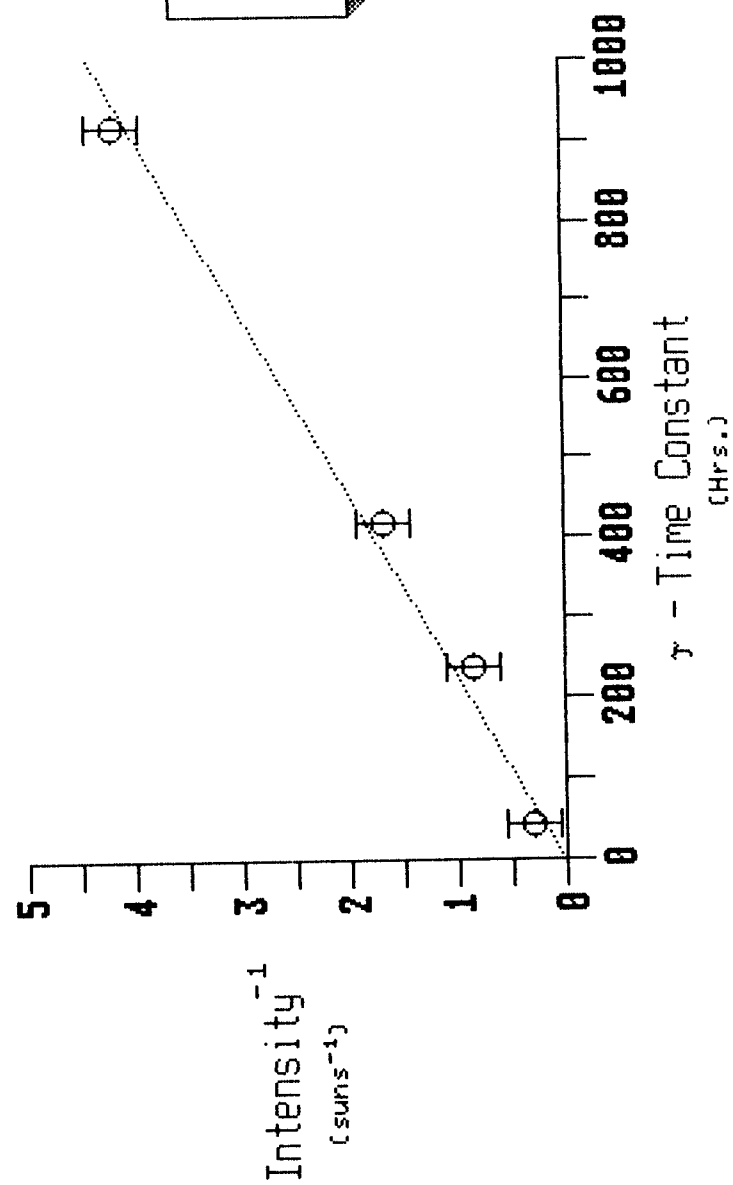


Figure 6. Inverse linearity of τ with intensity

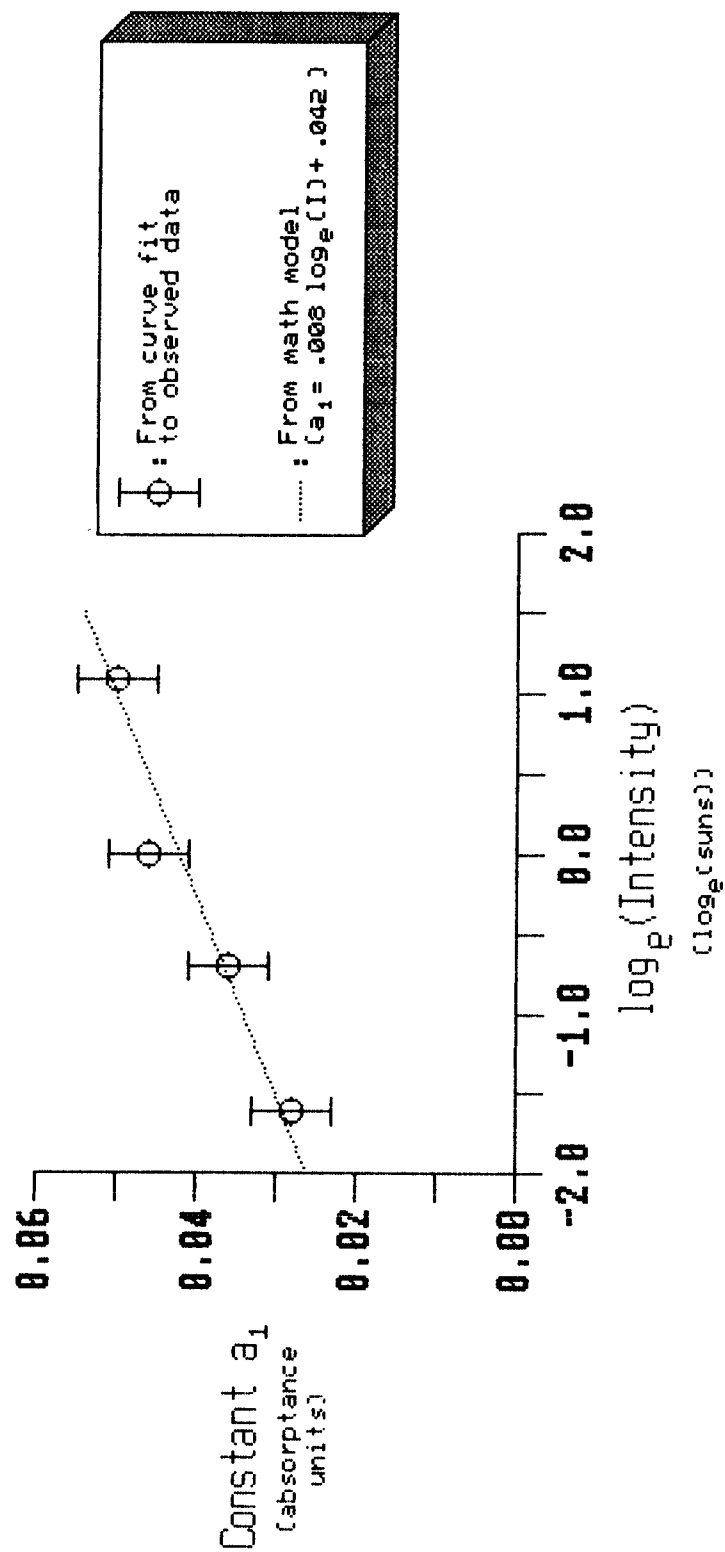


Figure 7. Linearity of a_1 with $\log_e(\text{intensity})$

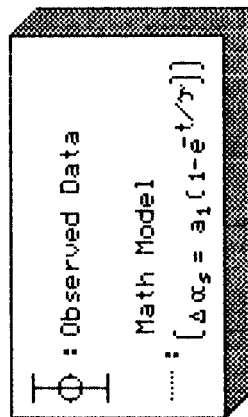
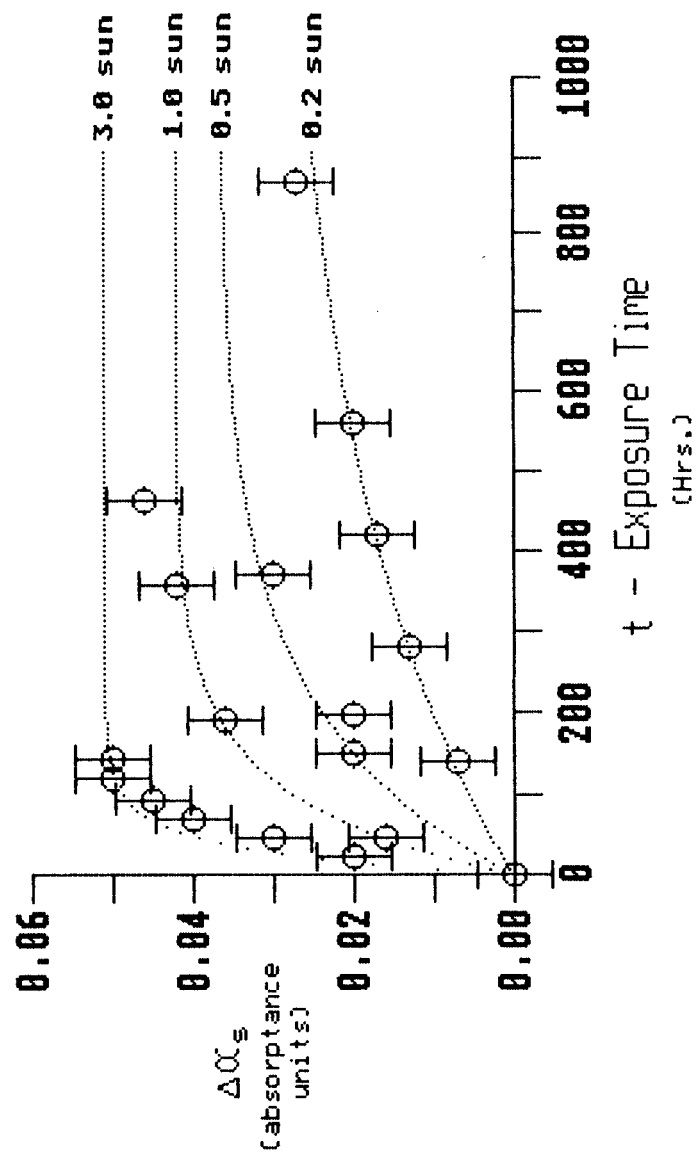


Figure 8. Observed data fit to math model